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19. ABSTRACT (Continue on reverse if necessary and identify by block number) This final report summarizes work carried out in a three year research program to develop efficient theoretical methods to study collisional processes involved in radiative signature modeling. The problems of rotational, vibrational and electronic energy transfer have been studied using novel semiclassical methods. The developed advancements in techniques are generally applicable to a state-to-state description of gas phase and gas/surface collisions leading to radiating species.					
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CONTROLLING BOOST PHASE SIGNATURES

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## **I. Statement of Problem**

For strategic defense, it is important to be able to effectively model radiative signatures<sup>1</sup> arising from interaction of missiles and space vehicles with the atmospheric and exhaust environment. This requires accurate kinetic description of dozens of reactive and inelastic molecular collisional processes whose cross sections or rates have to be known. Experimental methods of obtaining these kinetic parameters are not by themselves cost-effective since theory can be accurate, is often needed for insight into experimental designs, and the required supercomputers are becoming more available. Nevertheless, for realistic applications, exact theoretical methods do strain supercomputer performance limits and there exists a need for efficient approximate theoretical methods for which existing computers are adequate.

Once these practically reliable approximate theoretical methods are validated they may be used to routinely calculate collisional mechanisms and cross sections at a state-to-state level of detail in realistic, and practically important gas and gas/surface collisions. The present research goals were to develop, validate, and illustrate promising semiclassical methods of scattering theory based on the eikonal method. For applications to gas and gas/surface collisions, these semiclassical methods can reduce the computational effort for any given size molecules and thereby enable larger systems to be studied which would be beyond existing supercomputer performance if one were to use exact methods.

## **II. Summary of Important Results**

Exciting new advances have been made in this three year research program to establish the important role to be played by semiclassical methods in studying gas and gas/surface collision problems. The following subsections introduce the specific semiclassical methods adopted in this work, and then describe the formal method developments made, the validation results obtained in comparison to exact quantal results, and useful production studies that already go beyond the capability of "exact quantum dynamics plus supercomputers". A final subsection discusses computational studies conducted for diffusion and reaction on surfaces. This study used standard quasiclassical trajectory methods to study surface recombination dynamics; it also involved using the new embedded diatomics in molecules (EDIM) method to generate potential energy surfaces for N and O atoms diffusing and O atoms recombining on Ni surfaces. A three-dimensional gas/surface collision code capable of treating reactive events and semiclassical dynamics of diatom inelastic collisions at surfaces has been developed in this part of the effort. This code can be used to correlate energy accommodation at surfaces and the production of excited species in the gas phase due to gas/surface interactions.

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<sup>1</sup> This research effort was supported as a part of the SDIO Boost-Phase Signatures subtask.

## A. Introduction

The three year research summarized here employed two distinct types of semiclassical methods: (1) a method in which the system is divided into a classical part and a quantum mechanical part with the former's dynamics being determined by multiple potentials describing the effect of the latter part and (2) a method in which the quantum mechanical interference effects are incorporated by employing semiclassical wavefunctions constructed from classical trajectories. Method (1) is very convenient for incorporation of classical thermal motion of substrate atoms during a gas/surface collision as well as for the inclusion of quantized phonon effects. However, it entails large basis expansions in vibrational and rotational quantum degrees of freedom. The resultant restricted size-scalability implies a restriction on the number of degrees of freedom whose motion may be explicitly included in a quantum mechanical fashion; for e.g., the treatment of diatomic rotations and vibrations at surfaces is already a formidable problem if the surface motion also plays an active role.

Method (2) is new and can be used fruitfully whenever approximate semiclassical wavefunctions prove adequate. We briefly review its historic development. Although the semiclassical approach was seriously developed in the US during the seventies, it soon went out of use due to unforeseen computational difficulties. Two of the unique difficulties of implementing Miller's classical S-matrix theory were (1) the need to perform a nonlinear root-trajectory search in order to determine solution trajectories that connect specified initial and final quantal states (states between which the collision induced transitions of interest occur) and (2) the need to relate action-angle variable descriptions to cartesian variables (This was required to translate interaction potentials and semiclassical wavefunctions into a common set of variables). The developments of the seventies have thus remained a formal contribution that awaited a suitable computational vehicle for practical implementation.

There were parallel developments in the USSR, mainly contained in the work of Maslov on semiclassical wavefunctions, their mathematical existence conditions and their propagation. This work remained largely unknown in the US till the recent translation of Maslov's work appeared.<sup>2</sup> Maslov's work was in contrast to the approach in the west which was based on the theory of the classical S-matrix.<sup>3</sup> Maslov established criteria for the existence of semiclassical solutions and

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2. V. P. Maslov and M. V. Fedoriuk, "Semiclassical Approximation in Quantum Mechanics", D. Reidel, Boston (1981).
  3. W. H. Miller, J. Chem. Phys. **53**, 1949 (1970); Adv. Chem. Phys. **25**, 69 (1974); Adv. Chem. Phys. **30**, 77 (1975).

detailed procedures to be used to propagate the multidimensional semiclassical wavefunctions and extract observables. The recent review by Delos<sup>4</sup> is a succinct presentation of Maslov's approach.

The present research employs semiclassical methods based on the eikonal approach and was inspired by some of Marcus's ideas<sup>5</sup> in the seventies dealing with the semiclassical wavefunction. Since observables are calculated here from knowing the semiclassical wavefunctions, our framework draws its ultimate mathematical roots from Maslov's work. However, exact semiclassical wavefunctions are not easily calculated in spite of following the Maslov procedure, because rigorously, this involves Fourier transforming the problem between coordinate and momentum spaces depending on where the caustic lies. Whenever a change of sign in a component momentum is encountered, the trajectory is close to the multidimensional caustic in configuration space and one transforms to momentum space. The reverse transformation should be carried out after a local half cycle in the momentum space. This can be computationally very intensive and hence undesirable for our main goal of developing a practically useful approximate dynamical method. Therefore, one of the tasks in this research has been to develop approximate methods of evaluating semiclassical wavefunctions without performing frequent and expensive Fourier transformations. Furthermore, it is notable that our approach does not involve nonlinear root trajectory searches or the intervention of action-angle variables which were jointly responsible for the failure of the computational implementation efforts of the seventies.

## **B. Theoretical Methodology Development**

### *Semiclassical Wavefunctions*

Fortunately, it is possible to use approximate methods of evaluating semiclassical wavefunctions without having to perform frequent and expensive Fourier transformations. This is possible for systems where simplifying criteria become applicable rendering them similar to the cases where the well-known WKB turning point continuation rules for semiclassical wavefunctions become a good approximation. The present approximation is to pretend that *a priori* time scale separability holds at caustics between different degrees of freedom (for purposes of propagating the phase of the wavefunction) so that WKB phase-continuation rules may be applied for each individual degree of freedom. It must be stressed here that the classical dynamics controlling the time evolution of the phase is treated exactly (not assuming any separability) - only the precise point of time when the phase discontinuity associated with traversing the caustic enters the calculation is approximated.

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4. J. B. Delos, Adv. Chem. Phys. **65**, 161 (1986).

5. R. Marcus, J. Chem. Phys. **54**, 3965 (1971); *ibid* **59**, 5135 (1973).

The validity of the above approximate approach must be tested for different classes of collision problems, and once validated, could be used with confidence. The resultant numerical procedure scales like classical mechanics with the number of degrees of freedom and hence is quite inexpensive for the problems on hand. The applications to be studied must be formally analyzed in the initial stage. This has to be done periodically as new applications are encountered. We describe our validation work of this approach on the single potential surface problem of O+HF collisions in a subsection below.

### *Multisurface Dynamics*

We have extended<sup>6</sup> the original formal framework of the eikonal approach due to Micha<sup>7</sup> in several important ways although these extensions are yet to be numerically tested. Briefly, the important extensions include: (1) a more general definition of the effective potential that is thus no longer restricted to the Ehrenfest form, and (2) a multiple trajectory theory known as the Adiabatic Velocity Field Method (AVFM) where exact adiabatic trajectories are used away from the nonadiabatic coupling region. The AVFM dynamical equations are determined by neglecting terms of order  $\hbar^2$  from the Schroedinger equation whereas the adiabatic velocity field is defined to zeroth order in  $\hbar$ . A theorem has been proven showing that the initial conditions for the quasiperiodic degrees of freedom should be chosen the same for all adiabatic surfaces in such a calculation. In the AVFM, unlike in the original work of Micha, the final state is not an average state but satisfies the scattering boundary condition with well-defined momentum components in each of the channels and hence is physically more realistic.

It is clear that these new computational methods will need appropriate formal adaptation for different classes of dynamical problems as they arise, e.g., depending on which degrees of freedom, electronic, vibrational, surface phonon, etc., are treated quantum mechanically, or half collision versus full collision, or reactive versus nonreactive scattering. Following these periodic formal developments as needed, the intrinsic components of our approximate method development research effort are in two stages:

(1) validation of technology for problems for which quantum mechanical methods are feasible and benchmark results are available, and

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6. G. A. Natanson and P. K. Swaminathan, "Semiclassical Methodology for Computing Multichannel Eikonal Wavefunctions in Molecular Collisions - A Reformulation and Extension", Chemical Dynamics Technical Report (1989).

7 D. A. Micha, J. Chem. Phys. **78**, 7138 (1983)

(2) application to problems for which quantum mechanical methods are difficult or infeasible using available computer resources.

The transition to stage 2 is to be necessarily based on intuition and extrapolation of experience within a certain class of problems. The progress achieved in these two stages within this contract are summarized below.

### **B. Research to Validate New Methodology (Stage 1)**

We were in stage (1) for most of the problems studied in this three year period. Thus our computational work was on problems or models for which exact results for making comparisons were available. Our key validations were dramatically successful and included studies of (1) rotationally and electronically inelastic scattering of NO from Ag(111) surfaces<sup>8</sup> and (2) vibrational excitation of HF in collisions with O atoms.<sup>9</sup> We summarize only the latter work which was recently submitted for publication.

Semiclassical wavefunctions were computed for vibrationally inelastic scattering during O+HF collisions in the infinite order sudden (IOS) approximation. Due to the existence of previous quantum results,<sup>10</sup> the d=2 IOS model provided a convenient multidimensional example required to validate the approximate evaluation of phase continuation through caustics. The semiclassical results for vibrational excitation were in very good agreement with the exact results. The agreement was found superior for excitations higher than  $v=0$  to  $v=1$  although even the latter result improved by using the time-reversed propagation starting in  $v=1$ . The time-reversed results for higher excitations agreed well thereby satisfying time reversal better than  $v, v'=0, 1$ . Typically, results converged within 50-100 trajectories for each column of the S-matrix. A dependence of the results on the exact point in space where the S-matrix integral was defined was suitably averaged out by a numerical smoothing.

The success of the approximate multidimensional vibrationally inelastic semiclassical wavefunction is very significant because it dramatically extends their utility beyond previous validations<sup>11</sup> based on photodissociation cross sections. Photodissociation cross sections can

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8. B. M. Rice, B. C. Garrett, P. K. Swaminathan, and M. H. Alexander, J. Chem. Phys. **90**, 575 (1989).
  9. G. A. Natanson and P. K. Swaminathan, submitted to Chem. Phys. Lett. (1990).
  10. M. J. Redmon, L. T. Redmon, and B. C. Garrett, AFRPL TR-84-030, "Collisional Excitation Cross Sections," Sec. 3, (1984).
  11. P. K. Swaminathan, C. D. Stodden and D. A. Micha, J. Chem. Phys. **90**, 5501 (1989).

reflect only the behavior in the Franck-Condon region whereas vibrational excitation tests the full inelastic scattering wavefunction resulting from dozens of traversals through the caustic. Now the method may be extended to other vibrational excitation problems such as the three-dimensional atom/diatom, diatom/diatom, atom/triatom, etc. collisions. Along the same lines we have already developed the formalism to evaluate the semiclassical wavefunction for rotational scattering at surfaces (such as the NO/Ag(111) problem) that is usually studied by expensive expansion methods.

### C. Generation of Results using New Methodology (Stage 2)

As an example of a quantum mechanically infeasible study, we cite our work<sup>1 2</sup> on electronically inelastic gas/surface collision dynamics, where we obtained results for temperature-dependent O(<sup>1</sup>D) quenching at model surfaces. This study starts to go beyond today's capability limits of exact quantum dynamics on supercomputers. The idea illustrated in ref. 12 was one of combining a classical stochastic dynamical model for the surface with a semiclassical description of electronic inelasticity in a primary region. Further development of this type of application may be conducted in close interaction with experiments from which empirical information about interaction of different electronic states may be extracted; this is desirable and required because *ab initio* quantum chemistry methods are not yet in a position to routinely provide the required interaction information in gas/surface systems. Limited *ab initio* calculations and empirical modeling of potential surfaces should be combined to obtain semiquantitative data on the gas/surface processes.

In another study,<sup>13</sup> we have extended our flat (averaged) surface calculations of NO/Ag(111) to include surface corrugations. Corrugation effect on the rotational inelasticity was found to be significant. The high-J and low-J rainbows in the scattered intensity were found to depend on the specific site (atop, bridge, and three-fold sites were examined) where the diatom impacts. This provides very detailed site-dependent information on the effects of anisotropy on rotational inelasticity that can be very useful in refining the potential energy surface. This type of detail can be more easily obtained from semiclassical rather than quantal calculations by examining the trajectory evolution. Modern experimental techniques are starting to sense molecular orientation dependence of rotational scattering patterns. Interpretation of such experiments are also easily done in terms of these semiclassical calculations. Foremost of all, lattice temperature effects may be readily included in the semiclassical framework and these studies may be extended to study surface temperature sensitivity.

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12. P. K. Swaminathan, B. C. Garrett, and C. S. Murthy, *J. Chem. Phys.* **88**, 2822 (1988).

13. P. K. Swaminathan, G. A. Natanson and C. Y. Lee, to be published.



#### D. Other Gas/Surface Studies

During this contract, due to the tremendous interest seen in the chemistry of air species (N, O based) we generated gas/surface interaction models for O and N atoms diffusing on Ni surfaces and two O atoms recombining on these surfaces.<sup>14</sup> The goal was to be prepared for dynamics calculations involving these species pertaining to the Boost-Phase program. These models are empirical in nature and are based on the embedded diatomics in molecules (EDIM) approach. EDIM uses a judicious combination of the embedded atom method (EAM) developed at Sandia Laboratory and the diatomics in molecules (DIM) method from gas phase theory which are empirical schemes to represent potential energy surfaces in condensed metal phase and within the reactive primary zone respectively.

Calculations on surface diffusion of O and N were made using variational transition state theory (VTST). Diffusion was calculated<sup>14</sup> to be more efficient on Ni(111) than on Ni(100). Thus processes controlled by diffusion such as the Langmuir-Hinshelwood recombination have an advantage on the (111) than on the (100) surface. Dynamical calculations on O-atom recombination were conducted using quasiclassical trajectory method.<sup>15</sup> The latter calculations revealed detailed evolution of rotational and vibrational states during the recombination process leading to O<sub>2</sub> molecule produced in an excited vibrational state. The calculation also demonstrated the associated energy accommodation by the surface in relation to the amount of diatomic excitation. Illustrative calculations<sup>15</sup> indicated that more detailed and useful studies could be made along these lines as needed. The information from O and N atom interaction can be extended in the future to develop ground state potential surfaces for NO formation as well as NO<sub>2</sub> formation by recombination on Ni surfaces. The modeling of electronically excited states of these molecules that are usually produced at the high velocities of rocket-atmosphere interactions are, however, at present precluded due to lack of sufficient experimental or *ab initio* data to model the empirical surfaces. These excited states produced from surface-catalyzed reactions are believed to be the source of glow phenomena such as the shuttle glow and are likely contributors to Boost-Phase signatures as well.

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14. C. S. Murthy, B. C. Garrett, and P. K. Swaminathan, to be published.

15. P. K. Swaminathan, B. C. Garrett, and C. Y. Lee, unpublished results.

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2. B. M. Rice, B. C. Garrett, P. K. Swaminathan, and M. H. Alexander, "A Semiclassical Treatment of Rotationally-Electronically Inelastic Scattering of NO from Ag(111)", J. Chem. Phys. **90**, 575 (1989).
3. G. A. Natanson and P. K. Swaminathan, "Semiclassical Wavefunctions for Vibrationally Inelastic Scattering in the Time-Independent Picture", submitted to Chem. Phys. Lett. (1990).
4. C. S. Murthy, B. C. Garrett, and P. K. Swaminathan, "Potential Energy Functions and Dynamics of Atomic Oxygen and Nitrogen Interactions with Nickel Surfaces", submitted to J. Chem. Phys. (1990).
5. P. K. Swaminathan, G. A. Natanson, and C. Y. Lee, "A Semiclassical Treatment of Rotationally Inelastic Scattering of NO from Corrugated Ag(111) Surface", Chemical Dynamics Technical Report (1989), to be published.
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7. P. K. Swaminathan, B. C. Garrett and C. Y. Lee, "Trajectory Studies of Gas/Surface Chemical Energy Accommodation Dynamics", In preparation.
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### IV. Personnel

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